Alternative To Bisphenol A Based Epoxy Acrylates

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Abstract

Epoxy acrylates have had a successful and long history in the coatings industry due to their cost and performance advantages. However, the safety of bisphenol A-based epoxy resins has been questioned in various applications. Stepan has developed a new polyester polyol which, when acrylated, can be used as an alternative to epoxy based acrylates. The new product has coating properties that are similar to or exceed standard epoxy acrylate-based formulations including increased hardness, high gloss, great wear resistance and excellent chemical resistance.

Introduction

Epoxy acrylates are used in a wide variety of energy curable applications as these generally impart excellent hardness, gloss and chemical resistance. They can be used on a variety of surfaces including wood, plastic, concrete and metal. For general purpose applications, epoxy acrylates provide very good performance for a reasonable cost.

Epoxy resins based on bisphenol A (BPA) have been under scrutiny in several application areas.[1,2] Recently, California has implemented laws that ban BPA from baby bottles and sippy cups.[2] Other studies have claimed that extremely low levels of BPA do not pose a risk to human health.[3] Efforts are continuing to evaluate the effects of BPA based resins on the environment and human health.

Due to the additional attention to the BPA environmental and health issues, there is a need to develop products that do not use BPA. Stepan has developed a new polyol, Agent 3742-97, which, when acrylated, matches or exceeds the performance of two standard epoxy acrylates which are commonly used in various energy curable applications.

Experimental

The following ASTM methods were used to evaluate the coatings in this study:

Table 1. ASTM test summary.

Test	ASTM Method
Gloss	D523-08
Pencil Hardness	D3363-71
Cross Hatch Adhesion	D3359
Solvent Resistance	D5402
Fluorescent UV-Condensation Exposures of Paint and Related Coatings	D4587-01
Stain Resistance	D1308-02
Abrasion Resistance	D4060-95

Two general purpose commercial epoxy acrylates, Control I and Control II, were compared against the new polyester acrylate based on Agent 3742-97.

A new polyester polyol, Agent 3742-97, has been developed by Stepan that can be used for UV coating applications. This polyol has a hydroxyl value of 311 mg KOH/g, calculated functionality (eq OH/mol) of 3.6 and a viscosity of 3969 cP at 60°C.

Results and Discussion

Agent 3742-97 was acrylated and compared to two commercial epoxy acrylates, Control I and Control II, which were used in general purpose UV coating applications. Table 2 summarizes the properties of these three acrylates.

Table 2. Acrylate characterization

Acrylate	Base	Calculated Functionality (eq. acrylate/mol)	Viscosity (cP) @ 60°C
Acrylate A	Agent 3742-97	3.6	888
Control I	Bisphenol A epoxy	2	4569
Control II	Bisphenol A epoxy	2	4300

Although Acrylate A has higher functionality than the epoxy acrylates used in this study, it has lower viscosity. Lower viscosity along with higher functionality is a desired property. To obtain lower viscosity bisphenol A acrylates, monomers need to be added or structural modifications are required. Agent 3742-97 based acrylate has inherently low viscosity and this does not require additional monomers to lower the viscosity.

Initial evaluations were done by comparing the three acrylates using the same amount of each acrylate in the formulation. Table 3 details the coating formulations used for this part of the investigation.

Table 3. Coating formulation

Material	Weight Percent
Acrylate Resin	25
Tri(propylene glycol) diacrylate (TPGDA)	30
Trimethylolpropane triacrylate (TMPTA)	28
Difunctional amine coinitiator	10
Photoinitator I	2
Photoinitator II	3
Photoinitator III	1
Leveling agent	1

Formulation viscosities were measured for each. Note that the Acrylate A formulation was significantly lower than the two commercial acrylate formulations, (Figure 1).

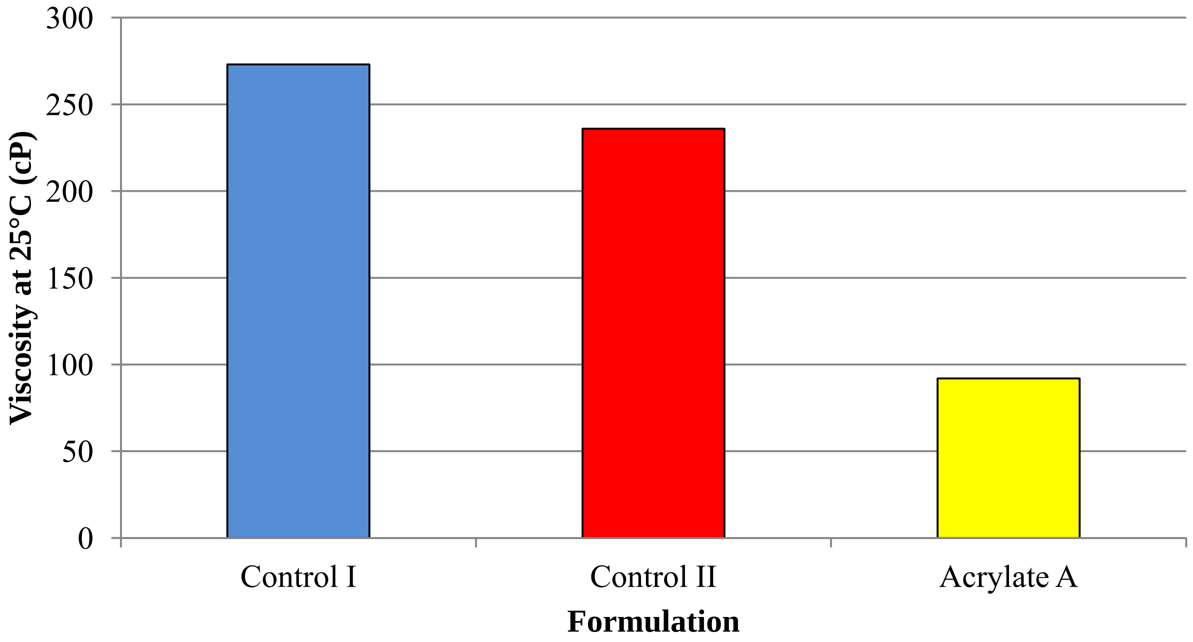

Figure 1. Formulation viscosities (cP) at 25°C.

All coatings were made using a 2.5 mil draw down bar and cured at different speeds to evaluate differences in performance. Table 4 shows the light intensity measurement for different curing speeds.

Table 4. Curing speeds and light intensity at each speed

Speed (ft/min)	Light Intensity (mJ/cm^2)
60	176
120	90
180	63
210	59

Cured coatings were subjected to various tests. Cross hatch adhesion was evaluated for each formulation to see how well these coatings bonded to different substrates including MYLAR® film, stainless steel and aluminum (Figures 2-4).

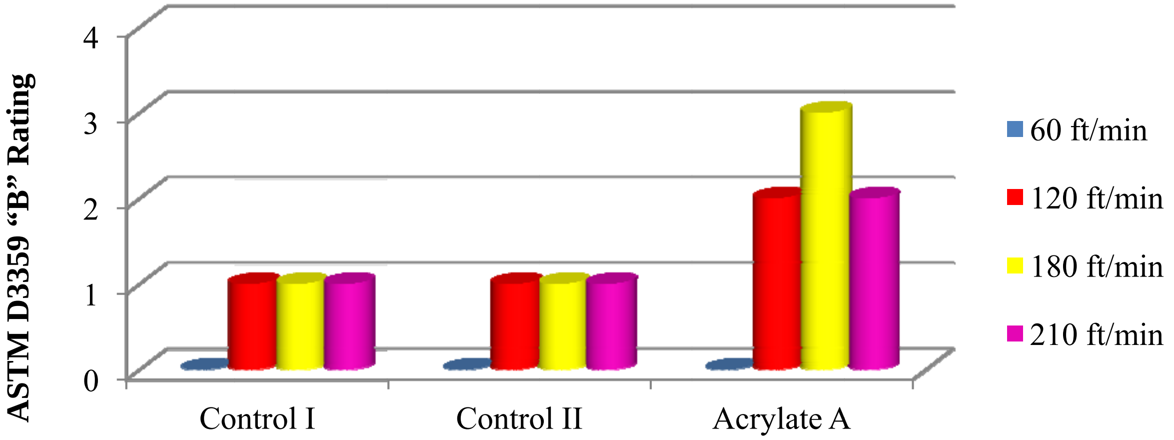

Figure 2. Cross hatch adhesion results based on cure speed-MYLAR film.

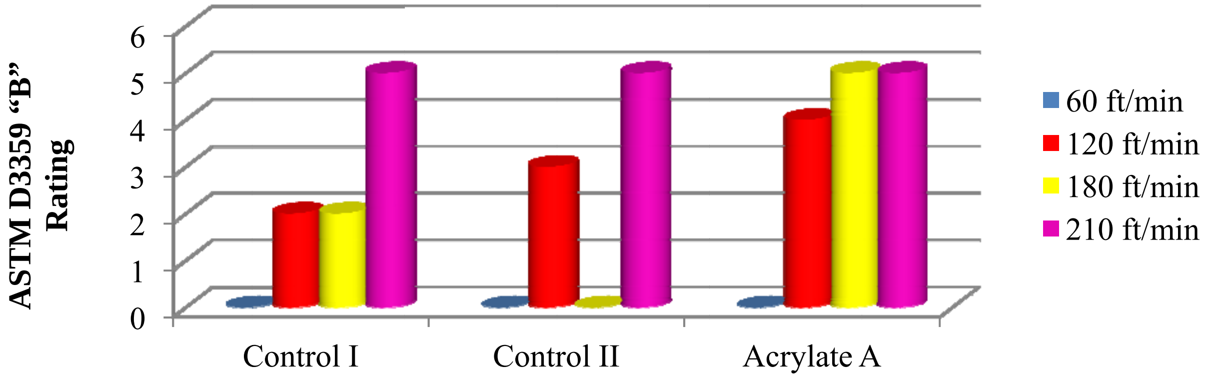

Figure 3. Cross hatch adhesion results based on cure speed-Stainless steel.

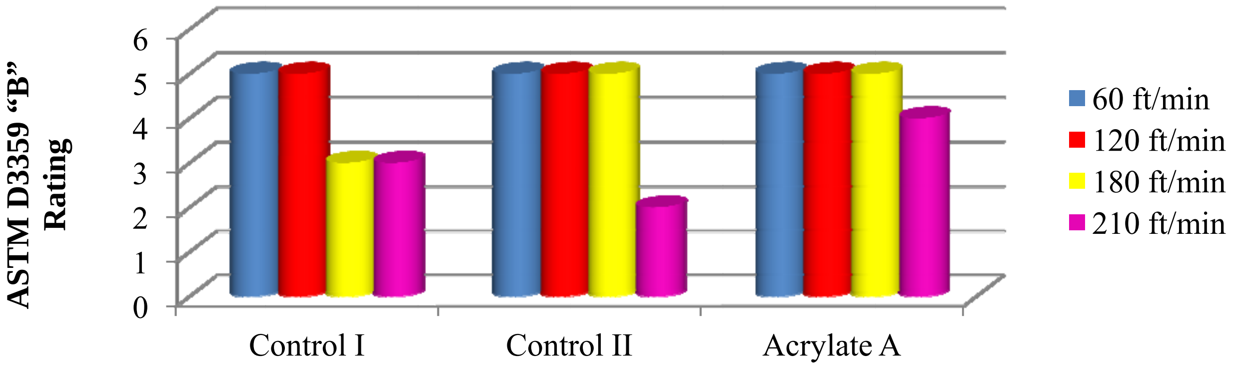

Figure 4. Cross hatch adhesion results based on cure speed-Aluminum.

For the MYLAR and stainless steel coating that were cured at 60 ft/min, poor cross hatch adhesion results were seen. This may be due to the coating shrinkage occurring at higher degree of curing compared to the faster speeds. This may also be due to internal stress within the coating resulting in poor adhesion when cured at this speed.

On MYLAR film, the formulation using the Stepan based polyol acrylate had better cross hatch adhesion than the two commercial epoxy based formulations at higher curing speeds. The adhesion results for the two metal substrates showed that the Acrylate A based formulation was better than the two commercial epoxy acrylate formulations. The data shows the Acrylate A based formulation had better cross hatch adhesion to these three substrates.

Abrasion resistance is a very important quality for coatings that will experience heavy traffic. Abrasion results from TABER® Abraser are in Figure 5.

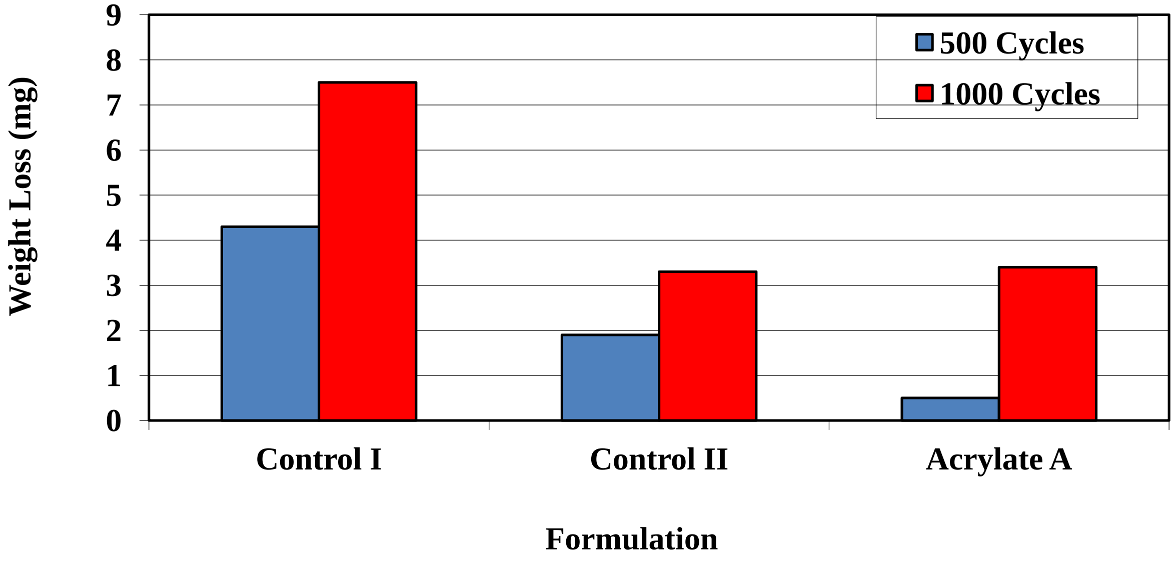

Figure 5. TABER Abrasion resistance results at curing speed of 60 ft/min.

Acrylate A based formulation had lower weight loss than the Control I based formulation and lower weight loss after 500 cycles compared to the Control II formulation. At 1000 cycles, the Acrylate A based and Control II formulations were approximately the same. Overall, the TABER abrasion experiments showed that the Acrylate A formulation had lower weight loss and comparable or even better abrasion resistance than the two epoxy acrylate formulations.

The pencil hardness of each coating was also examined. The results are shown in Table 5.

Table 5. Coating pencil hardness at different curing speeds.

Curing Speed (ft/min)	60	120	180	210
Acrylate A	6H	6H	6H	6H
Control I	6H	6H	6H	5H
Control II	6H	6H	6H	5H

Note that the Stepan polyol based acrylate had a pencil hardness that was slightly higher than the two control epoxy acrlylate formulations at the higher curing speed.

Chemical resistance of a coating is one of the most important coatings performance characteristics. Chemical resistance was evaluated for each coating cured at different speeds. Here, double rub resistance testing with isopropyl alcohol (IPA) was used to test the chemical resistance (Figure 6).

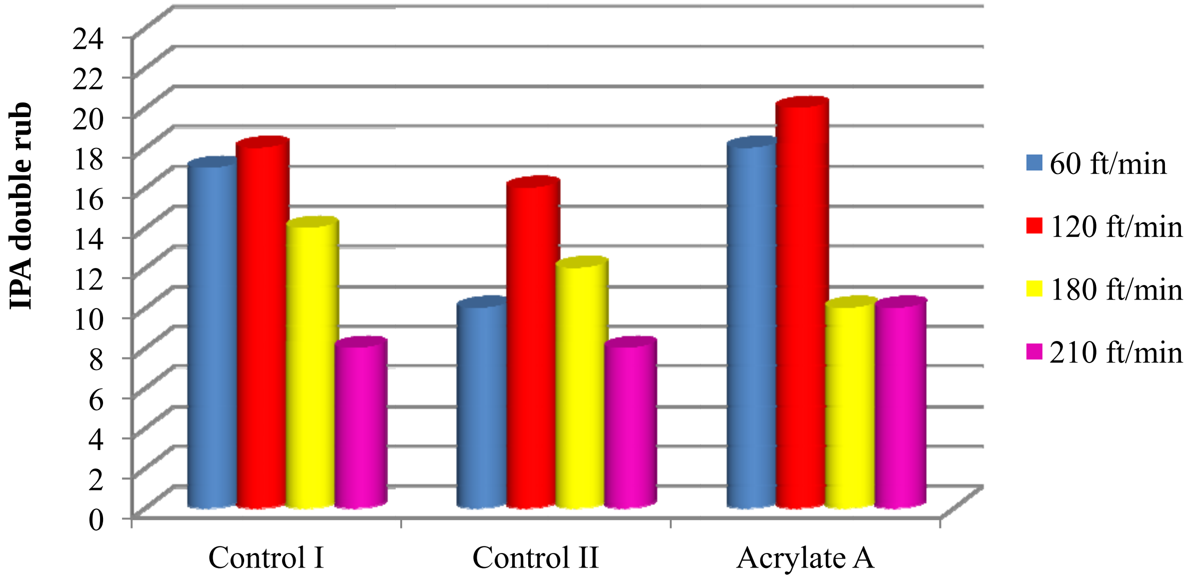

Figure 6. Isopropyl alcohol (IPA) double rub resistance.

The results show that the Stepan polyol acrylate formulation was comparable to the epoxy coatings at different curing speeds.

Since coatings are used in many outdoor applications, the gloss and yellowing of the cured samples was evaluated. Each coating was exposed to light, heat and humidity according to the ASTM D4587-01, Cycle #1 method. The duration of exposure for these coatings samples was 1000 hours; films were cured at 210 ft/min. The gloss and yellowing indexes (average of three) were evaluated before and after the exposure, Tables 6 and 7, respectively.

Table 6. 60° Gloss after 1000 hours of aging using ASTM D4587-01, Cycle #1.

Coating Base	Before (Standard Deviation)	After (Standard Deviation)	60° Gloss Change
Acrylate A	90.7 (±0.4)	94.8 (±0.9)	+4.1 (±0.76)
Control I	92.0 (±0.3)	95.1 (±0.3)	+3.1 (±0.3)
Control II	91.9 (±0.4)	96.0 (±0.3)	+4.1 (±0.35)

Table 7. Yellowness index after 1000 hours of aging using ASTM D4587-01, Cycle #1

Coating Base	Before (Standard Deviation)	After (Standard Deviation)	Yellowness Index Change
Acrylate A	7.45 (±0.12)	5.97 (±0.24)	-1.48 (±0.19)
Control I	7.82 (±0.21)	6.89 (±0.22)	-0.93 (±0.21)
Control II	7.87 (±0.17)	6.35 (±0.10)	-1.57 (±0.14)

Tables 6 and 7 show statistically significant differences ($\alpha < 0.01$ level of significance paired t-tests) in gloss and yellowness index with all samples, suggesting additional curing and photo bleaching. The amount of gloss increase was essentially the same for all samples ($\alpha > 0.1$). The yellowness index decrease was also nearly the same for all samples except where Acrylate A yellowed less than Control I ($\alpha < 0.05$). Control I and II films had higher yellowness indexes after exposure compared to Acrylate A films. Based on the statistical analysis, Acrylate A coatings were very similar to the epoxy acrylate based coatings.

Protecting substrates against stains is also a desirable property for protective coatings. The stain resistance for each coating was also evaluated (Table 8).

Table 8. Stain resistance (16 hrs.) results for each coating.

Coating Base	D.I. Water (25°C)	Boiling Water	Ketchup	Coffee
Acrylate A	5	5	5	5
Control I	4	5	5	5
Control II	4	5	5	5

The stain results show that the Acrylate A based coating was slightly better than the two commercial epoxy acrylate coatings. Thus, in the formulations used in this investigation, Acrylate A had very good stain resistance compared to the two epoxy acrylate based coatings.

Further Evaluation-Equalized Viscosity Formulations

In a further evaluation of Acrylate A, three new formulations were developed that would have nearly the same viscosity. These formulations were developed to simulate a more representative formulation that might be used in an energy curable coatings application. This was done by adjusting the amount of TPGDA in each formulation so that the final formulation viscosities were nearly the same (Table 9). The pencil hardness, aluminum adhesion, gloss, chemical resistance and abrasion resistance were evaluated using these formulations.

Table 9. Coating formulations with similar viscosities. Weight percentages are shown.

Material	Formulation A (Acrylate A)	Formulation B (Control I)	Formulation C (Control II)
Acrylate Resin	26.00	18.75	19.50
Tri(propylene glycol) diacrylate (TPGDA)	29.00	36.25	35.50
Trimethylolpropane triacrylate (TMPTA)	28.00	28.00	28.00
Difunctional amine coinitiator	10.00	10.00	10.00
Photoinitator I	2.00	2.00	2.00
Photoinitator II	3.00	2.00	2.00
Photoinitator III	1.00	1.00	2.00
Leveling agent	1.00	1.00	1.00
Final Viscosity @ 25°C (cP)	142	138	140

Since Acrylate A's viscosity is less than the two epoxy acrylates, more of this oligomer can be used in a coatings formulation with nearly the same viscosity as the two epoxy acrylate viscosities Having the option to increase the oligomer amount in a formulation should enhance the performance properties of the final coating.

Table 10 summarizes the pencil hardness testing results for each formulation at different curing speeds.

Table 10. Coating pencil hardness results at different curing speeds.

Curing Speed (fpm)	60	120	180	210
Acrylate A	6H	6H	6H	5H
Control I	5H	5H	5H	4H
Control II	6H	6H	6H	5H

The Acrylate A formulation had either the same or higher pencil hardness than the two control formulations using the commercial epoxy acrylate standards. Although, Acrylate A is a polyester acrylate, the hardness was nearly the same as the two commercial epoxy acrylates. This could be the result of a larger amount of the oligomer in the formulation and/or higher functionality of Acrylate A.

The cross hatch adhesion on aluminum was evaluated for each formulation, Figure 7.

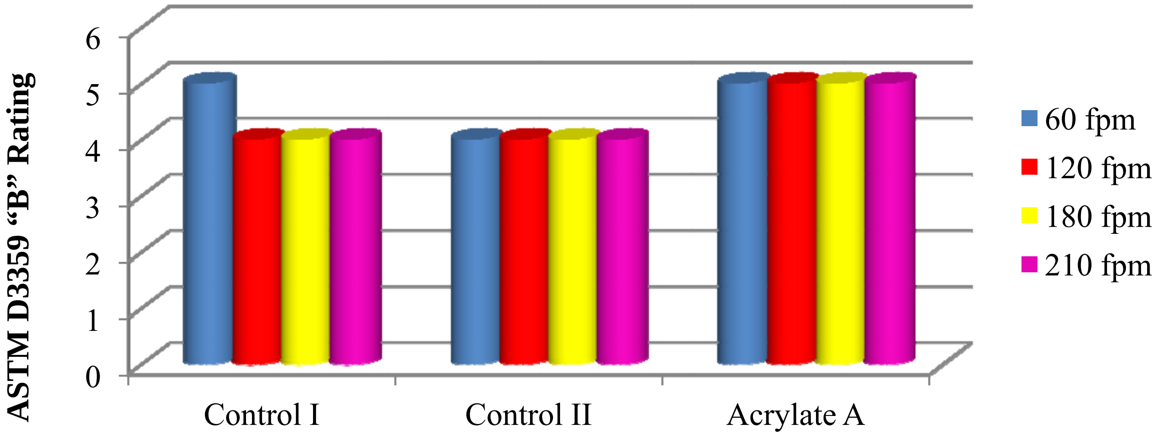

Figure 7. Cross hatch adhesion (aluminum) for coating formulations cured at different speeds.

Acrylate A had better adhesion results overall than the two epoxy acrylate formulations at nearly all the curing speeds tested.

Coatings were applied to Leneta charts to measure the 60 degree gloss of each coating. These coatings were cured at 60 feet per minute. The 60 degree gloss measurements were 93 for Acrylate A formulations and 94.5 for the two epoxy acrylate formulations. The 60 degree gloss results for the Acrylate A formulation was nearly the same as the epoxy based formulations.

The chemical resistance for each coating was tested using an isopropanol (IPA) double rub test and a staining test, Figure 8 and Table 11 respectively.

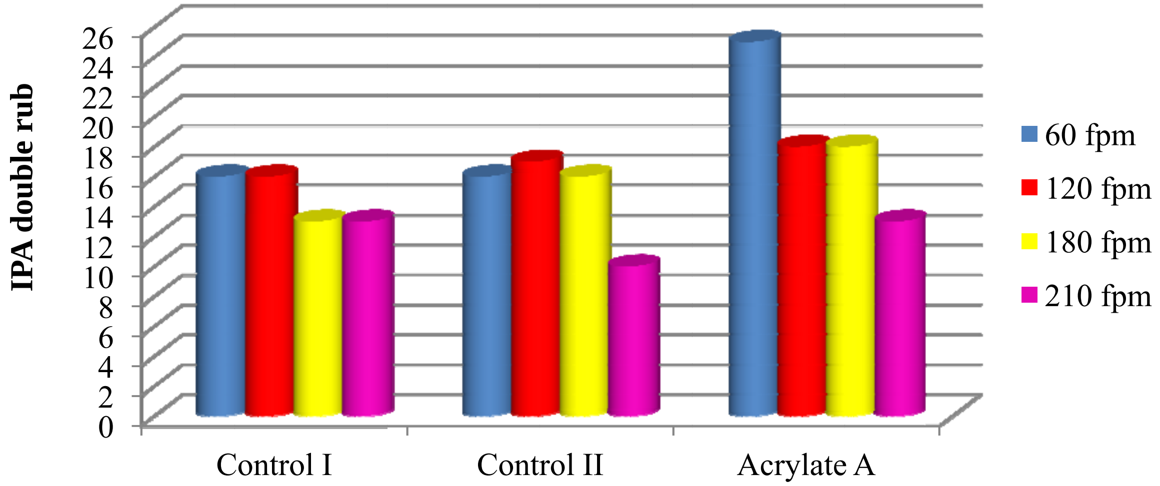

Figure 8. IPA double rub results at different curing speeds.

Table 11. Staining resistance of the coatings cured at 210 feet per minute.

Coating Base	D.I. Water	Boiling Water	Ketchup	Coffee
Acrylate A	4	4	5	4
Control I	4	4	5	4
Control II	4	4	5	4

The IPA double rub results show that the A formulation was better than both control formulations using epoxy acrylates. The stain results also shows that Acrylate A had the same stain resistance than the epoxy acrylate formulations. These results could be due to the higher amount of Acrylate A resin in this formulation which would presumably give better properties due to the higher oligomer content. However, if the same amount of epoxy acrylate was used, then the overall formulation viscosity would be higher, which may be a drawback in some applications.

Finally, all three coatings were evaluated for abrasion resistance after curing at 60 feet per minute, Figure 9.

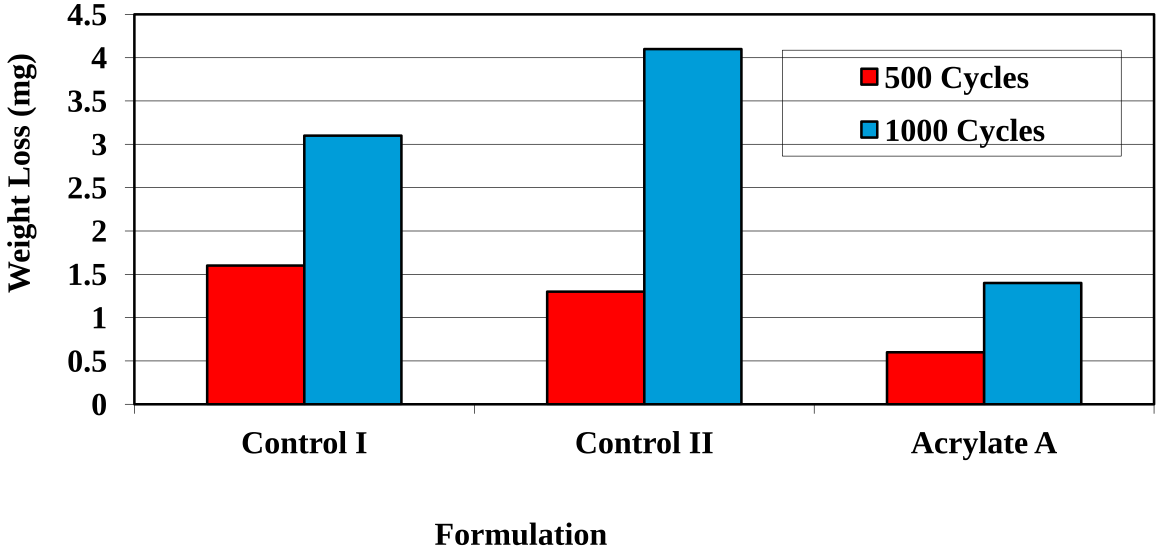

Figure 9. Taber abrasion results for each coating cured at 60 feet per minute.

The Acrylate A based formulation had better abrasion resistance than the two epoxy formulations. Abrasion resistance was much better at 500 and especially at 1000 cycles. Although each formulation had similar pencil hardness at this curing speed, the Acrylate A formulation still had better abrasion resistance than the corresponding epoxy acrylate formulations.

Conclusions

The polyester acrylate made from Agent 3742-97 provides comparable or better performance when compared directly with two general purpose commercial epoxy acrylate formulations. This acrylate had lower viscosity than the corresponding epoxy acrylates allowing formulators greater processing latitude without sacrificing most performance attributes. When it is was compared in a formulation with nearly the same viscosity, a larger amount of the Agent 3742-97 oligomer could be used which resulted in better performance characteristics than the two epoxy acrylate formulations. Agent 3742-97 has an excellent balance of hardness and flexibility that can provide very good coating characteristics in energy curable coating applications.

When Agent 3742-97 was compared directly to the two epoxy acrylates, better cross hatch adhesion with most substrates was seen along with better abrasion resistance. Exposure results also show slightly less yellowing compared to the two epoxy coatings. Comparable results were seen with pencil hardness, gloss (after exposure), stain resistance, and chemical (IPA double rub) resistance.

In the coating formulations that had similar viscosities, Agent 3742-97 acrylate formulations were better than the two epoxy formulations. This formulation did not require additional mononmer to reduce the viscosity to an acceptable level which resulted in better coating properties. Overall, the performance of the polyester acrylate of Agent 3742-97 indicates that it might be an appropriate substitute for the two commercial general purpose epoxy acrylates when used in energy curable formulations.

Appendix

The authors would like to thank Kip Hillshafer for his assistance with statistical analysis of the data that was taken.

All formulations were cured on a Fusion UV System, Inc. F300S/SQ lamp system and LC-6 benchtop conveyor with a single mercury lamp. All coatings were cured using a single pass and were made using a 2.5 mil draw down bar. Coating sample for mechanical testing were made using a 20 mil draw down bar. A UV Power Puck made by EIT was used to measure the lamp intensity. Gloss measurements were done using a BYK Gardner Micro-TRI-Gloss Meter at room temperature using ASTM Method D523-08. Abrasion resistance measurements were done using a TABER Industries Abraser, model 5130. All color development measurements were done using a Hunter Lab Color Quest XE colorimeter.

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